the two roots of Equation 2 for zero *s-p* separation and the curves B and C of Fig. 7 the roots of Equation 2 with 1.84 e. v. *s-p* separation. To test the extent to which neglect of $\Delta_{\mathrm{I\,II}}$ can be compensated by suitable choice of values of the energy exchange integral $H_{\mathrm{I\,II}}$, we may evaluate $H_{\mathrm{I\,II}}$ as a function of ρ by substituting for $H_{\mathrm{I\,I}}$ and $H_{\mathrm{II\,II}}$ in Equation 1 their values as given by curves 2*s* and 2*p*, respectively, of Fig. 2 and choosing values of $H_{\mathrm{I\,II}}$ which cause curve *B* of this figure to represent the low root of the equation. The expression for $H_{\mathrm{I\,II}}$ found in this way can then be used to evaluate the low root of Equation 1 for the case of 1.84 e. v. *s-p* separation. It is found that over the range 2.5 to 3.5 for ρ curve C as calculated in this way differs from the curve given by Equation 2 by less than 0.05 e. v. (4% of the bond energy). This provides some justification for the use of Equation 1 in place of Equation 2 for rough calculations in which the magnitude of the exchange integral is determined empirically.

We are indebted to Dr. S. Weinbaum and Mrs. M. R. Lassettre for assistance with the calculations described in this report.

Summary

Theoretical energy curves for one-electron bonds between two atoms are calculated for bond orbitals formed by hybridization of 2*s* and 2*p* orbitals, 3*s* and 3*p* orbitals, and 3*s*, 3*p*, and 3*d* orbitals, the same radial part being used for the orbitals in a set. It is found that for *s-p* hybridization the bond energy is closely proportional to S^2, with *S* the magnitude of the angular part of the bond orbital in the bond direction. This relation is less satisfactorily approximated in the case of *s-p-d* hybridization.

It is shown that the energy of a normal covalent bond A-B between unlike atoms is probably represented more closely by the geometric mean of the bond energies for A-A and B-B than by their arithmetic mean.

The energy of the one-electron bond in the lithium molecule ion is calculated with consideration of the *s p* separation to be 1.19 e. v., and the hybrid bond orbital involved is shown to involve about equal contributions from the 2*s* and 2*p* orbitals of the lithium atom.

PASADENA, CALIF. RECEIVED JUNE 1, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

The Mechanism of the Dehydration of Calcium Sulfate Hemihydrate. II. Observations with Large Crystals

BY HARRY B. WEISER AND W. O. MILLIGAN

In the first communication[1] under this title it was demonstrated that: (1) contrary to the conclusions of Linck and Jung, Balarew, Gibson and Holt, and others, the dehydration curve of calcium sulfate hemihydrate has a definite step indicating that the compound is a true chemical hydrate and not a zeolite; (2) contrary to the conclusions of Jung, Ramsdell and Partridge, Caspari, Gallitelli, Onorato, and others, calcium sulfate hemihydrate and dehydrated hemihydrate (soluble anhydrite) are not identical in structure as evidenced by the existence of characteristic differences in the X-radiograms of the two substances.

At about the same time that the above results were reported, Caspari,[2] in a second paper, reached diametrically opposite conclusions from an X-ray examination of large crystals of hemihydrate grown from a nitric acid solution. In the first place, he claims that the proposed arrangement of three molecules of calcium sulfate in a hexagonal unit cell will not suit a definite hydrate of the composition $CaSO_4 \cdot 0.5H_2O$; and in the second place, he states that X-ray rotation spectrograms of the opaque anhydrous pseudomorph obtained by dehydrating the so-called hemihydrate were in every way identical with those of the original hemihydrate.

In view of these conflicting reports, it becomes a question of fact whether macrocrystals of hemihydrate such as used by Caspari behave the same or differently from microcrystals obtained by dehydration of $CaSO_4 \cdot 2H_2O$. The following experiments attempt to answer this question.

Experimental

Preparation of Large Crystals of $CaSO_4 \cdot 0.5H_2O$.—To prepare large crystals Caspari dis-

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[1] Weiser, Milligan and Ekholm, THIS JOURNAL, **58**, 1261 (1936).

[2] Caspari, *Proc. Roy. Soc.* (London), **155**, 41 (1936).

solved precipitated $CaSO_4\cdot 2H_2O$ in warm 50 to 60% nitric acid and kept the solution at 80 to 90° until a crop of crystals was obtained. At the outset we attempted to make the crystals by saturating 300 cc. of approximately 55% nitric acid with precipitated dihydrate and allowing the solution to stand at 85°. By this procedure we obtained large crystals which proved to be anhydrous and which gave the same X-ray diffraction pattern as the mineral anhydrite. This meant that either the nitric acid concentration or the temperature was too high to form hemihydrate. The latter compound was obtained pure and in quantity with 55% nitric acid at 50°. The following procedure was found to be particularly satisfactory: to a mixture consisting of 221.7 cc. of 15.8 *M* nitric acid, 26.7 cc. of 1.819 *M* sulfuric acid and 26.2 cc. of water at 50° was added slowly 25.38 cc. of 1.917 *M* calcium nitrate. The resulting clear solution in a glass-stoppered flask was placed in a hot-air oven at 50° for several days until a crop of macrocrystals 1–2 mm. in length was obtained. After decanting the mother liquor, the crystals were washed thoroughly with 95% alcohol by the aid of the centrifuge, pressed between filter paper, and bottled.

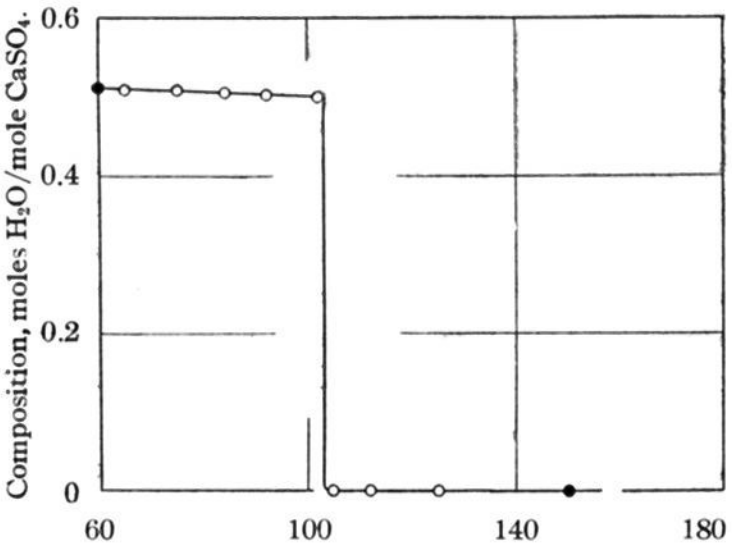

Fig. 1.—Dehydration isobar for macro-crystals of $CaSO_4\cdot 0.5H_2O$: ○, sample 1; ●, sample 2.

Isobaric Dehydration of $CaSO_4\cdot 0.5H_2O$.—The macrocrystals prepared as described above were subjected to isobaric dehydration at an aqueous vapor pressure of 23.6 mm. The procedure was identical with that already given.[1] The important point was to make certain that equilibrium was attained at each temperature. If there was no change in weight on successive weighings eighteen to twenty-four hours apart, it was assumed that the system was in equilibrium at that temperature. The results of the observations are shown graphically in Fig. 1. The isobar breaks sharply at a temperature just above 100° indicating that the compound is not a zeolite but a true hemihydrate identical with that obtained by dehydration of $CaSO_4\cdot 2H_2O$. The break in the dehydration curve is sharper and appears to come at a slightly higher temperature than was observed with submicroscopic crystals of hemihydrate prepared by dehydration of selenite.

X-Ray Diffraction Examination.—The large crystals still wet with alcohol were ground in an agate mortar, placed in a 0.5-mm. Mark tube, and the X-ray diffraction pattern obtained with a Philips tube using Cu K_α radiation filtered through nickel foil. Diffraction patterns were also obtained for the sample dried at 60° and 23.6 mm. aqueous vapor pressure. The patterns for the samples undried and dried at 60° were identical and corresponded to that previously obtained[1] for $CaSO_4\cdot 0.5H_2O$.

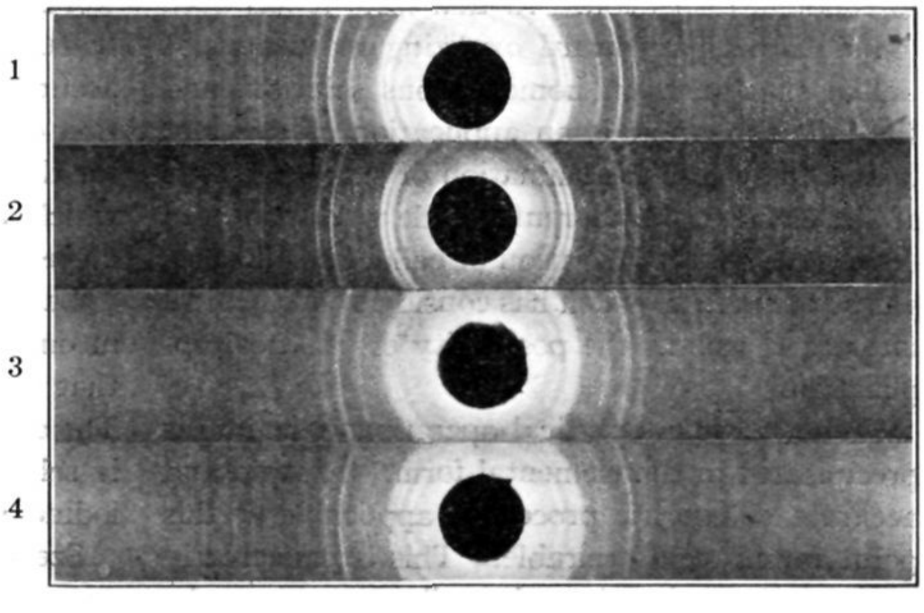

Fig. 2.—X-Ray diffraction patterns for: (1) $CaSO_4\cdot 0.5H_2O$ (submicroscopic crystals) prepared by dehydration of selenite; (2) dehydrated hemihydrate prepared by the dehydration of (1); (3) $CaSO_4\cdot 0.5H_2O$ (macrocrystals) prepared by the nitric acid method; (4) dehydrated hemihydrate prepared by the dehydration of (3).

Diffraction patterns for the dehydrated hemihydrate were obtained under conditions which prevented any possibility of rehydration. While still at a temperature above 100° a portion of the dehydrated sample was placed in a Mark tube which was subsequently kept at 130° in a vacuum for ten hours. The tube was then sealed off and the X-ray diffraction pattern obtained. The pattern was different in certain respects from the hemihydrate pattern but was identical with the dehydrated hemihydrate pattern obtained from the dehydration of selenite at 130°.[1] Reproductions of the negatives showing the X-ray diffraction patterns of hemihydrate and dehydrated hemihydrate are given in Fig. 2. Patterns 3 and 4, showing the spots, are for the large crystals of hemihydrate and dehydrated hemihydrate, respectively; 1 and 2 are the respective patterns for the submicroscopic crystals obtained by dehydration of selenite. These observations show once more that the crystal structure of hemihydrate is similar to but not identical with that of dehydrated hemihydrate. When these results are taken together with the isobaric dehydration data, they show conclusively that calcium sulfate hemihydrate is not a zeolite but a definite chemical individual, irrespective of the method of preparation or the crystal size.

In the light of the above observations one is forced to conclude that Caspari is not justified in his contention that calcium sulfate hemihydrate and dehydrated hemihydrate are identical. His experimental results are not satisfactory either because he could not detect the differences between the two preparations by means of X-ray rotation spectrograms or because his unspecified precautions against rehydration of the dehydrated sample were inadequate.

HOUSTON, TEXAS RECEIVED JUNE 1, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

The Quantitative Oxidation of Colloidal Selenium and its Application in the Volumetric Determination of Small Amounts of Selenium[1]

BY W. C. COLEMAN AND C. R. MCCROSKY

Selenium is an element that lends itself readily to colloidal dispersion. In this state it has been found to behave toward oxidizing reactants not unlike substances in homogeneous solution, and the following work is an application of this fact in the analytical determination of small amounts of the element. Apparently little work has been done on the direct titration of colloidal solutions, a type of reaction which has considerable chemical interest as well as the possibility of practical application.

Frequently in analytical operations selenium is precipitated in the elemental form. A rapid and accurate volumetric procedure applicable at this point would seem desirable. This is particularly true for the estimation of small amounts of selenium, a problem which recently has become of increasing importance. Such precipitates which would be free of interfering ions can be dissolved rapidly with a solution containing cyanide ion according to the reaction $CN^- + Se \longrightarrow SeCN^-$. When this reaction is reversed by adding an acid, red selenium precipitates and in the presence of a stabilizing agent remains in colloidal dispersion. It was found that the selenium in these colloidal solutions can be oxidized rapidly and quantitatively by certain volumetric oxidants. It seemed worth while to study the quantitative side of these reactions, first, with the idea of developing an accurate volumetric method for the determination of small amounts of selenium and, secondly, for the interest in chemical reactions of this kind which involve reactions between a solid in the dispersed phase and a reactant in true solution.

Lang[2] found that black selenium was oxidized incompletely by iodine monochloride but suggested that the red form might be oxidized successfully. The authors found that only in the colloidal state is selenium rapidly and completely oxidized by iodine monochloride.

Szebelledy and Schick[3] used colloidal selenium as an indicator in the bromate titration of arsenites.

Preparation of Materials

Pure selenium was prepared as described by Coleman and McCrosky.[4]

Sodium Selenocyanate.—A pure grade of sodium cyanide giving negative tests for ferricyanide and reducing agents was used for making the standard selenocyanate solutions by dissolving a weighed amount of the pure selenium with an excess of the salt and diluting to a definite

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[1] Original manuscript received April 29, 1936.

[2] R. Lang, *Z. anorg. allgem. Chem.*, **142**, 280 (1925).

[3] Szebelledy and Schick, *Z. anal. Chem.*, **97**, 186 (1934).

[4] Coleman and McCrosky, *Ind. Eng. Chem.*, **8**, 196 (1936).